

Supporting information for

## Ferroelectric Helical Polymer

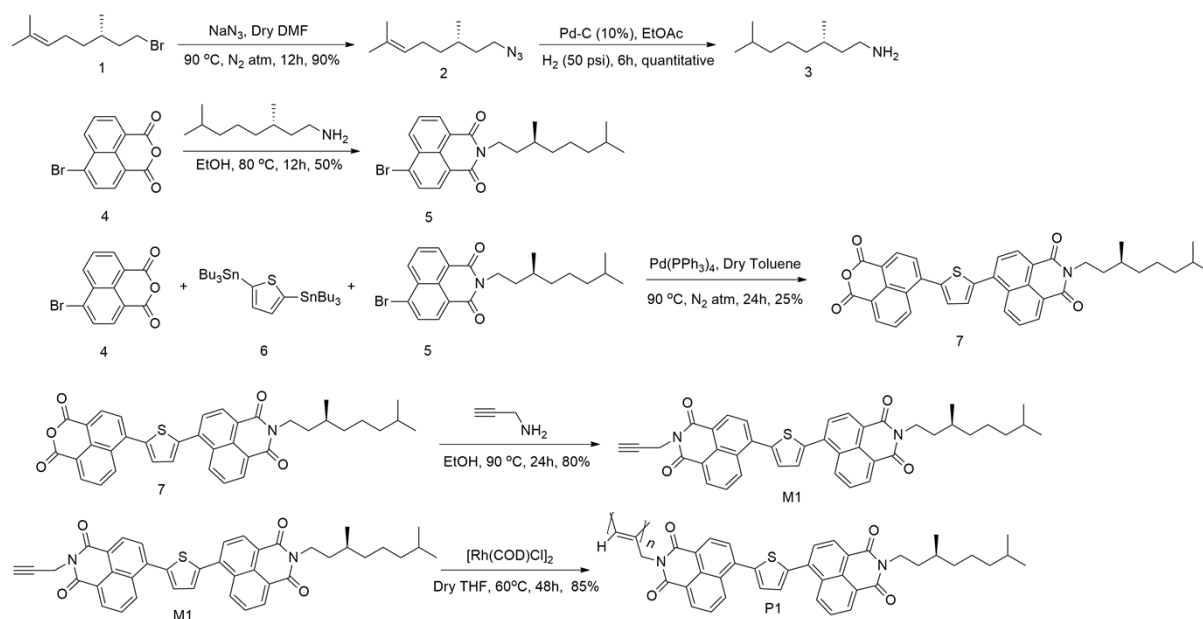
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**Materials and methods:** All the reagents and solvents were bought from commercial sources and purified by available standard procedures. <sup>1</sup> (*S*)-(+)-Citronellyl bromide, Pd-C (10%), 2,5-Bis(tributylstannyl)thiophene and Propargyl amine were purchased from Sigma-Aldrich. 4-Bromo-1,8-naphthalic anhydride, Pd(PPh<sub>3</sub>)<sub>4</sub> and [Rh(COD)Cl]<sub>2</sub> were purchased from TCI Chemicals. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded in Bruker DPX-300 MHz spectrometer. All the NMR peak positions were calibrated using TMS as an internal standard. Spectroscopy grade solvents were used for all physical and spectroscopic studies. FT-IR spectra were recorded using Perkin Elmer Spectrum 100FT-IR spectrometer. UV-Vis experiments were done in a JASCO V-750 spectrometer. Fluorescence emission spectra were acquired using Horiba FluoroMax3 spectrophotometer. Jasco J-815 Circular Dichroism (CD) Spectropolarimeter was used to carry out circular dichroism experiments. Size exclusion chromatography analysis of the polymers was done in THF (*c* = 5.0 mg / mL, flow rate 0.6 mL/min, *T* = 30 °C) in a Water's machine equipped with a 515 HPLC pump, Waters 2414 RI detector and HSPgel HT 4.0/HSPgel HT 2.5 columns connected in series and molecular weight and dispersity were estimated with respect to PS standards. TGA was recorded on a Netzsch STA449C thermal analyser in the temperature range of 25 °C-650 °C at heating rate of 10K/min. DSC was conducted by using TA instruments (DSC Q2000).



## Synthesis:

### Scheme S1: Synthesis of polymer P1.

**Compound 2 and 3** have been synthesized by us previously.<sup>2</sup>

**Synthesis of compound 5:** 4-Bromo-1,8-naphthalic anhydride (1.1 gm, 3.97 mmol) and compound 3 (0.8 gm, 5.086 mmol) were taken in a RB flask and ethanol (10 ml) was added into the reaction mixture. Then reflux was performed at 80 °C for overnight maintaining an inert N<sub>2</sub> atmosphere. TLC was done in (30% DCM / Hexane) solution and relatively non-polar desired product was clearly distinguished. The yellowish solid product was successfully separated out by column chromatography using silica gel (100-200) as stationary phase and 30% DCM-Hexane was used as eluent. Yield: 50%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ(ppm) = 8.66 – 7.84 (5H, m), 4.20 – 4.18 (2H, m), 1.73 – 1.12 (10H, m), 1.03 – 1.01 (3H, m), 0.86 – 0.84 (6H, m).

**Synthesis of compound 7:** Compound 4 (200 mg, 0.72 mmol), 5 (300 mg, 0.72 mmol) and 6 (472 mg, 0.72 mmol) were taken in a RB flask and dissolved in 10 ml anhydrous toluene. The mixture was bubbled with Ar gas for 15 min and then Pd(PPh<sub>3</sub>)<sub>4</sub> (170 mg, 0.14 mmol) was added into it under Ar atmosphere. Then reflux was performed at 90 °C for 24 hours under N<sub>2</sub> atmosphere. After the reaction was complete, excess toluene was evaporated in rotavapor and crude was solubilized in DCM-MeOH mixture. Then the desired product was purified by

column chromatography using silica gel (100-200) as the stationary phase and 90% DCM-Hexane was used as the eluent to obtain compound **7** as a red solid. Yield: 25%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$ (ppm) = 8.83 – 7.90 (10H, m), 7.51(2H, d), 4.24 (2H, m), 1.73 – 1.12 (10H, m), 1.02 (3H, d), 0.85 (6H, d).

**Synthesis of monomer M1:** Compound **7** (110 mg, 0.18mmol) was taken in 10 ml of ethanol and propargyl amine (100 mg, 1.8 mmol) was added into it. Then the mixture was refluxed at 90 °C for 24h. Then the reaction mixture was allowed to cool down to room temperature and diluted by 10 ml of ethanol further. The resulting solid precipitate was filtered and washed with ethanol a few times and dried under vacuum to get desired monomer as a red solid. Yield: 80%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$ (ppm) = 8.81 – 7.84 (10H, m), 7.50 (2H, s), 4.99 (2H, d), 4.21 (2H, m), 2.22 (1H, t), 1.75 – 1.12 (10H, m), 1.02 (3H, d), 0.85 (6H, d). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$ (ppm) = 164.44, 163.92, 163.47, 162.84, 142.39, 141.96, 138.73, 137.88, 132.58, 132.12, 132.07, 131.64, 131.24, 130.75, 130.09, 129.99, 129.83, 129.72, 129.12, 129.04, 128.93, 128.89, 127.68, 127.63, 123.36, 122.91, 122.71, 122.16, 78.57, 70.77, 39.41, 39.21, 37.29, 35.22, 31.43, 29.69, 28.07, 24.79, 22.76, 19.72. FT-IR (KBr pellet, wavenumber/cm<sup>-1</sup>): 3270 cm<sup>-1</sup> ( $\equiv$ C-H<sub>strc</sub>), 2122 cm<sup>-1</sup> (C $\equiv$ C<sub>strc</sub>).

**Synthesis of polymer P1:** Compound **M1** (100 mg, 0.15 mmol) was taken in a polymerization vessel and freshly dried THF (0.3 mL) was added into it and solubilized by gentle heating. Then the resulting solution was bubbled with Ar gas for 10 min. After that [Rh (COD)Cl]<sub>2</sub> (3.78 mg, 0.0077 mmol) was added into that vessel and bubbled the mixture with Ar gas for further 5 min. Then the obtained solution was stirred at 60 °C for 48h. After that, the heating was stopped and all the contents were diluted with additional 1.0 mL of THF and the resulting solution was precipitated from excess diethyl ether to obtain solid dark red polymer. Yield: 85%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$ (ppm) = 8.78 – 7.75 (broad), 7.50 (broad), 4.15 (broad), 1.73 – 0.85 (broad). Molecular weight (M<sub>n</sub>, from SEC, solvent: THF, PS standard) = 5600 g/mol (*D* = 1.10).

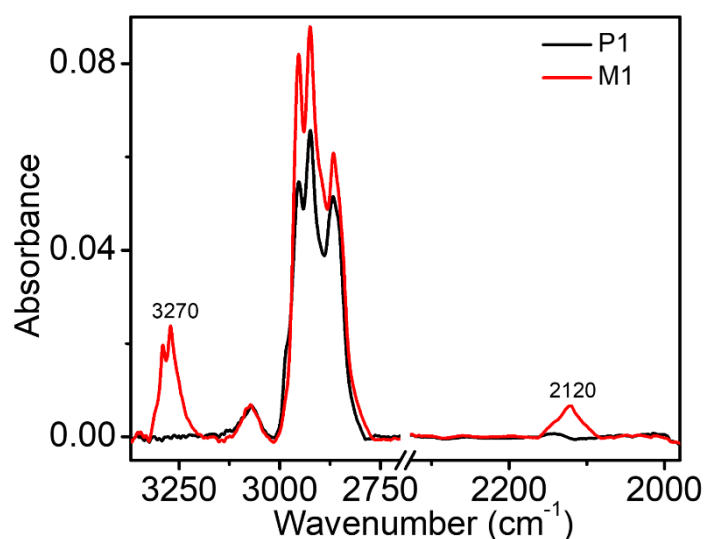
**Sample preparation for UV-Vis and CD experiments:** A stock solution of **P1** was prepared in spectroscopy grade THF at 1.0 mM (considering repeat unit molecular weight). From this stock, a measured amount was transferred to glass vial. Then the solvent was evaporated by heating with heat gun to get a thin film of the compound and measured amount of MCH-THF (90:10) was added to it as per volume and concentration needed for that particular experiment. Obtained solution was sonicated and heated gently in a water bath (65 °C) to get a homogenous solution which was allowed to stand at room temperature for 2h of equilibration time. In case of monomer **M1**, after evaporating THF to get a thin film, measured amount of MCH was

added to get the desired concentration needed for that particular experiment and was allowed to stand at room temperature.

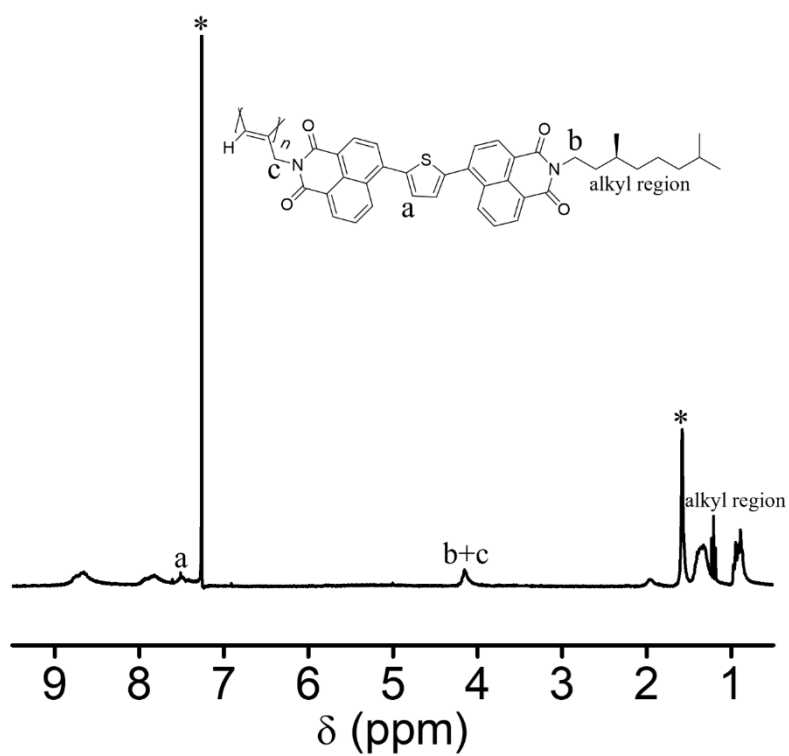
**Film and device preparation for dielectric, ferroelectric studies:** A 5.0 mM solution of **P1** was prepared in spectroscopy grade MCH-THF (90:10) through ultra-sonication at ambient temperature for 1h. ITO-coated glass slides ( $5 \times 5$  mm) with a surface resistivity of  $4 \text{ ohm}\cdot\text{m}$  (procured from Techinstro, India) was cleaned with deionized water, absolute ethanol, and acetone, followed by vacuum drying at room temperature. The film was then fabricated using the drop-casting technique and placed under vacuum for 48 hours to ensure complete drying. The thickness of the film for P-E loop measurement was determined to be approximately 0.12 mm, measured using a Mitutoyo Micrometer (Model No. 293-240-30) and for the PFM analysis  $\sim 500$  nm, which was precisely calculated using AFM (**Fig. S11**). Further, the ferroelectric and dielectric capacitor device was prepared by depositing Al-foil (Sigma Aldrich) on top of the film (electrode area  $\approx 0.94 \text{ mm}^2$ ) (Figure S5). Ferroelectric properties were measured with a Precision LCII Ferroelectric Tester (Radiant Technologies, Inc.) equipped with a microprobe station. Dielectric properties were recorded using impedance analyzer (HIOKI, IM 3536, LCR METER).

**PFM measurements:** Piezoresponse force microscopy (PFM) was conducted at ambient temperature using an Asylum Research MFP-3D atomic force microscope (AFM) equipped with a Ti/Ir (5/20) coated cantilever (ASYELEC-01, nominal spring constant of 2.0 N/m, and resonance frequency of 81 kHz). PFM phase and amplitude images, along with plots, were obtained at an applied bias voltage of  $\pm 5$  V. For the PFM experiment, a  $\sim 500$  nm thick film of the sample was prepared by drop-casting a 5.0 mM solution in MCH-THF (90:10) onto ITO-coated glass substrates as measured using AFM.

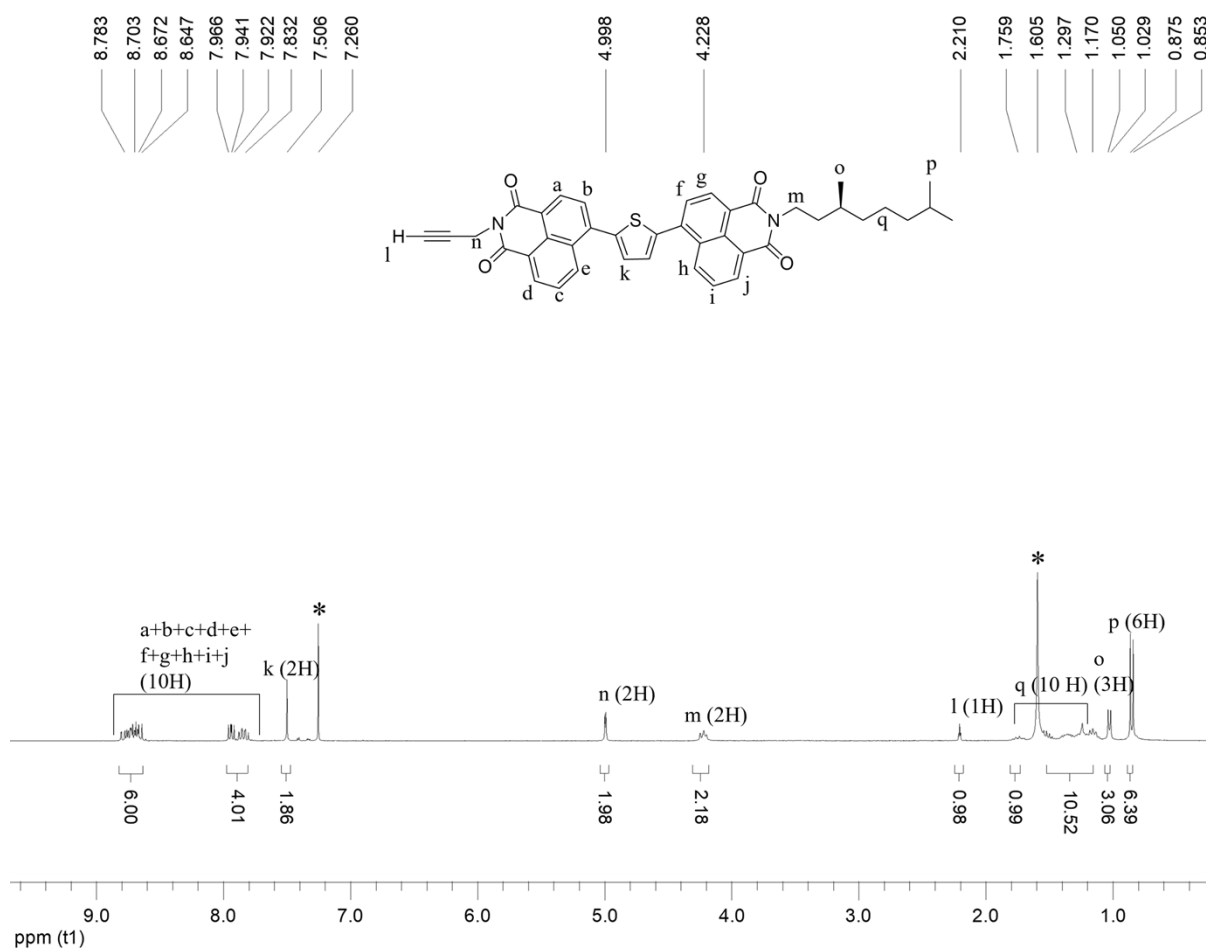
**Additional figures:**



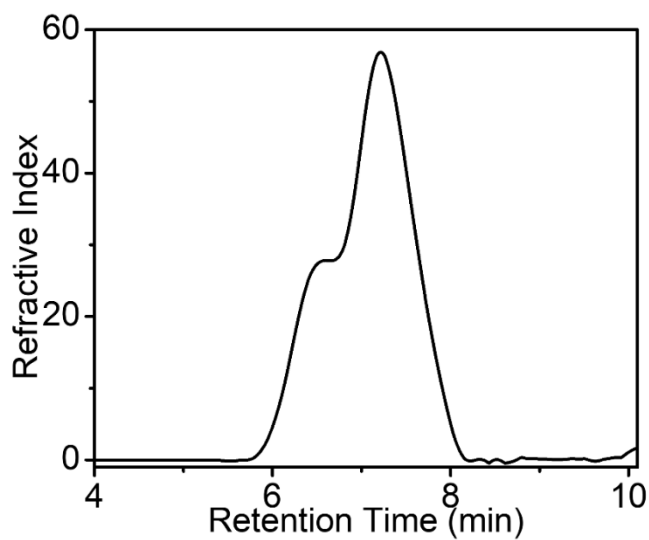
**Figure S1:** Solid state FT-IR spectra of both monomer (**M1**) and polymer (**P1**).



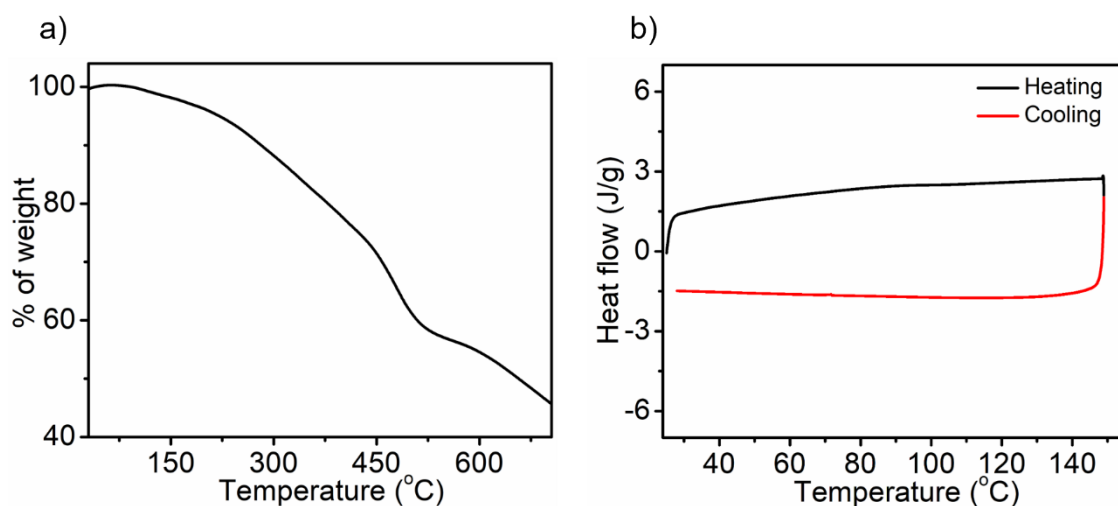
**Figure S2:** <sup>1</sup>H NMR of polymer **P1** in CDCl<sub>3</sub> (\* indicates residual solvent peak).



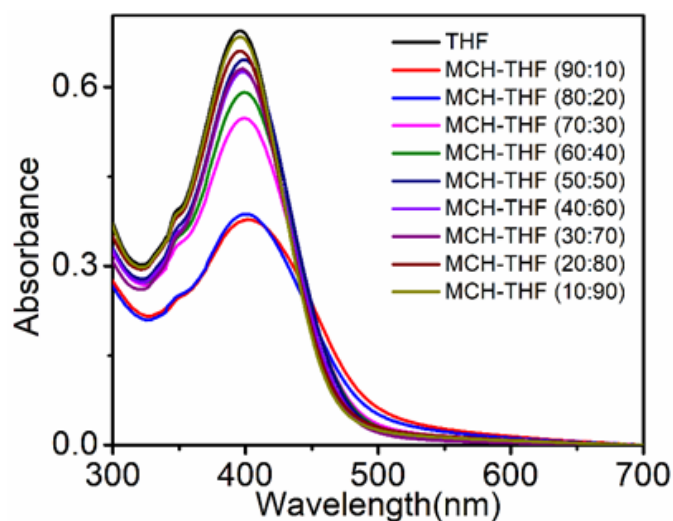
**Figure S3:**  $^1\text{H}$  NMR of polymer M1 in  $\text{CDCl}_3$  (\* indicates residual solvent peak).



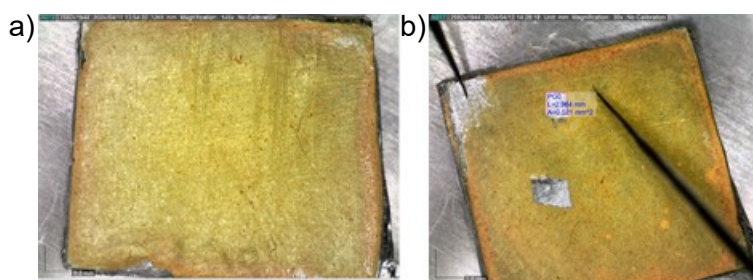
**Figure S4:** SEC traces of P1 in THF.



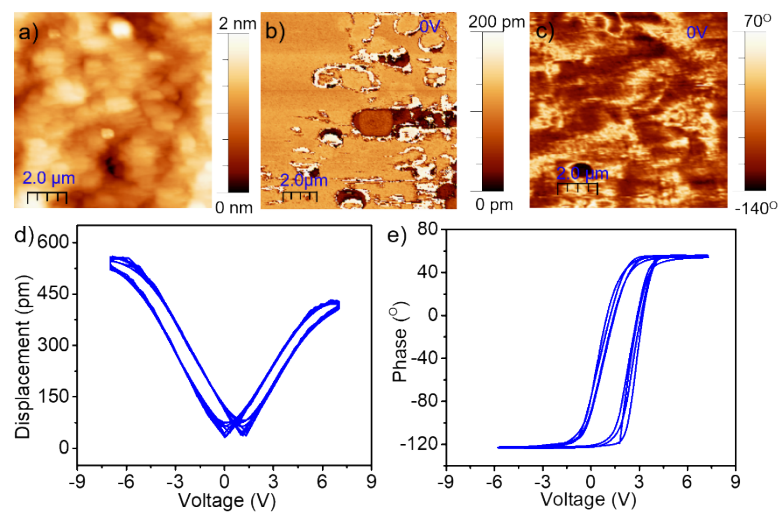
**Figure S5:** a) TGA and b) DSC traces of **P1**. TGA curve shows onset of weight-loss > 150 °C and hence DSC measurements could not be done beyond 150 °C.



**Figure S6:** UV-Vis study of **P1** in different MCH-THF ratio ( $c = 0.2 \text{ mM}$ ,  $l = 0.1 \text{ cm}$ ,  $T = 25 \text{ }^\circ\text{C}$ ).

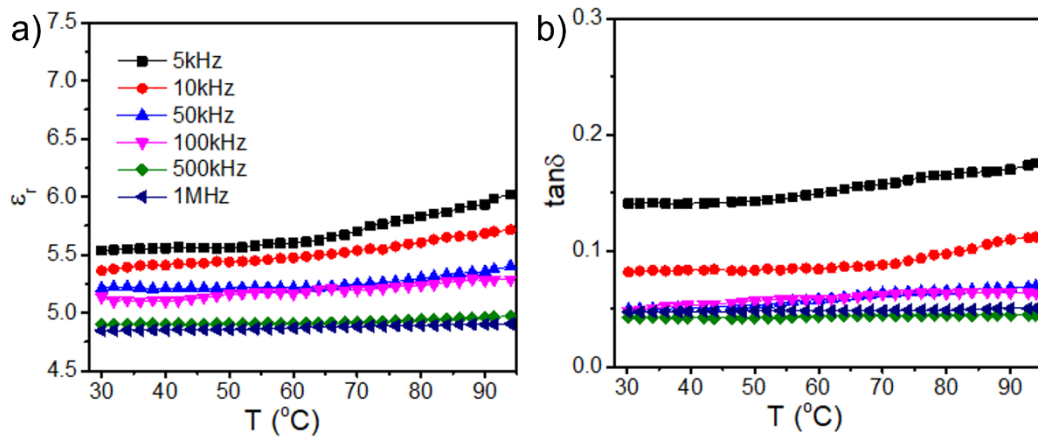


**Figure S7:** Representative drop-casted films on ITO-coated glass substrate. (a) thin film after 48h vacuum dry; (b) thin film and Al-foil as a top electrode.

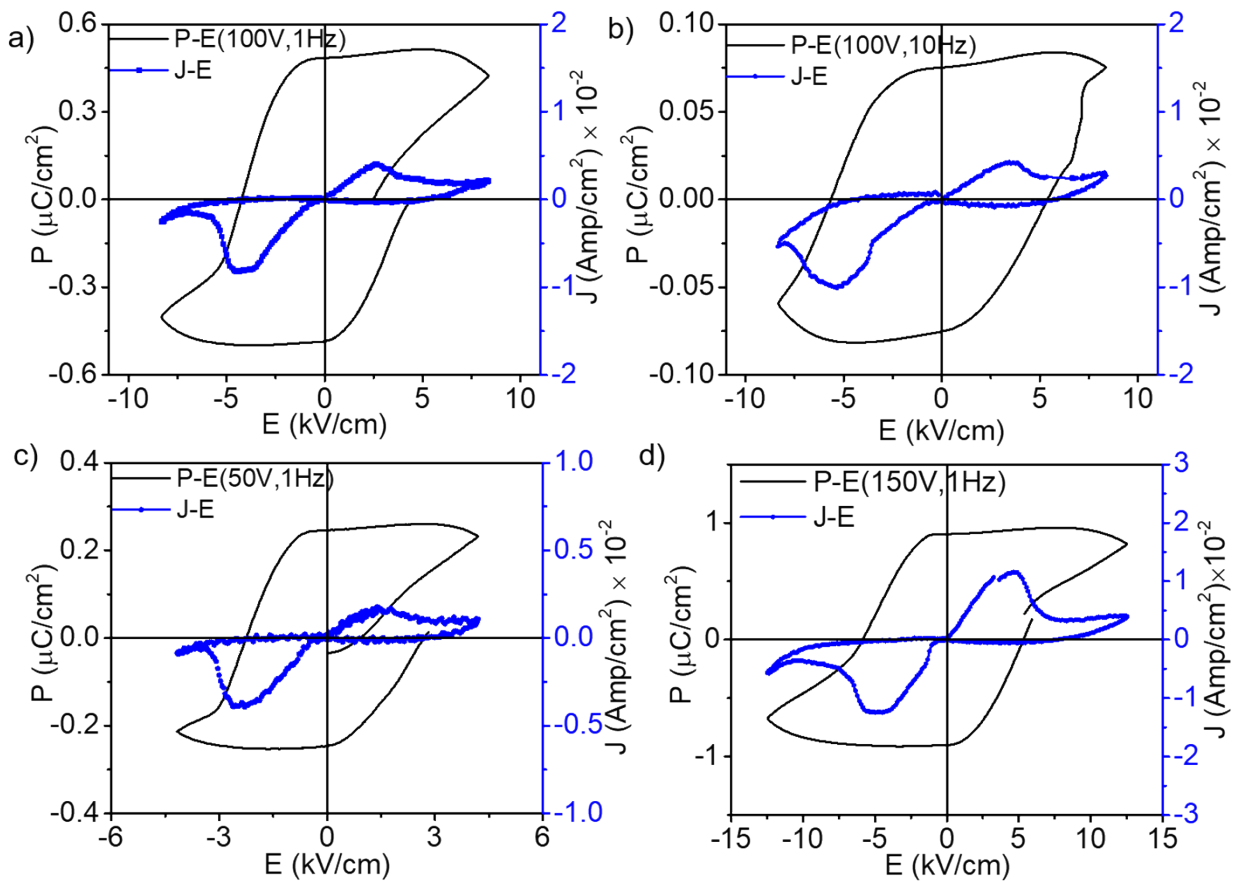


**Figure S8:** (a) Topography image in PFM measurement; (b) PFM amplitude; (c) PFM phase images of **P1** film at zero bias; (d, e) PFM butterfly and hysteresis loops at on-state.

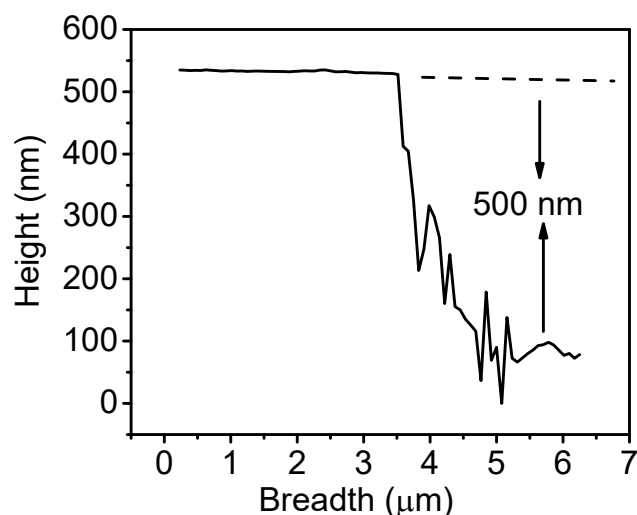




**Figure S9:** (a) Relative permittivity vs temperature plot upto 1MHz; (b) dielectric loss ( $\tan\delta$ ) of P1 film.



**Figure S10:** (a, b) Polarization vs electric field and corresponding current density vs electric field with different frequencies (1Hz to 50Hz) at applied voltage 100V. (c, d) polarization vs electric field and corresponding current density vs electric field with different voltage at 1Hz frequency.



**Figure S11:** Atomic force microscopy (AFM) measurements at RT of P1 film. Measurement was carried out in an Asylum Research Origin+ MFP-3D atomic force microscope (AFM) Oxford instruments with non-conductive Al (100) coating cantilever with non-coating Si tip of radius 7 nm (nominal spring constant 2.0 N/m, natural resonance frequency in air 70 kHz). The average thickness of the sample height was calculated to be ~500 nm.

**Table S1:** A comparison of piezo and ferroelectric parameters with recent organic materials.

Organic Piezo-Ferro systems	$d_{33}$ (pm/V)	$P_s$ ( $\mu\text{C}/\text{cm}^2$ )	$(P_r)$ ( $\mu\text{C}/\text{cm}^2$ )	Ref.
PVDF Nanofiber	3-7	-	-	ACS Appl. Polym. Mater. 2022, 4, 4751.
DBCz–TCNQ complex	33pC/N ( $d_{31}$ )	1.23	0.85	ACS Appl. Mater. Interfaces 2024, 16, 2583–2592
Nylon 11	6.5	-	-	Adv. Funct. Mater. 2021, 31, 2004326.
4,4'-Bpy/AcA	9.5	-	-	ACS Nano 2020, 14, 10704.
Amino Acids	11.4	-	-	ACS Appl. Mater. Interfaces 2022, 14, 46304.
BTA-C6-NDI <sub>3</sub>	5	-	-	Chem. Mater. 2023, 35, 3316.
Supramolecular polymer of ambipolar system	68 (on state)	1.9	0.9	Chem. Mater. 2023, 35, 6463-6471
(R)- and (S)-(N,N-dimethyl-3-fluoropyrrolidinium) iodide	-	0.48	0.4	Chem. Commun., 2020, 56, 7033.
amide-functionalized pyrene (Py) and naphthalene-diimide (NDI)	-	3.2	1.8	Chem. Commun., 2022, 58, 10508.
polyurethane (P1) and pyrene (Py)	-	0.8	0.12	Angewandte Chemie, 2022, 134(25), e202203817. <a href="https://doi.org/10.1002/ange.202203817">https://doi.org/10.1002/ange.202203817</a>
(Me <sub>2</sub> NH <sub>2</sub> )-[NaFe(CN) <sub>5</sub> (NO)],	-	1.65	0.7	J. Am. Chem. Soc. 2020, 142, 16990.
A1+DPT TIS–CT	-	4	1.1	J. Am. Chem. Soc. 2016, 138, 8259
[H-55DMBP][Hia],	-	1.2	0.7	Angew. Chem., Int. Ed. 2007, 46, 3497
[D55DMBP][Dia]	-	1.7	1.1	
Pyromellitic diimide-1 + 5-amino-1-naphthol -2	-	3.5	2.1	J. Am. Chem. Soc. 2017, 139, 9186
Donor-acceptor LASO complexes	-	2-6	1-1.5	Nature 488, 485–489 (2012)

DABCODA/LTa of DTa	-	0.45	0.42	Sci Rep 3, 2249 (2013). DOI: 10.1038/srep02249
$\alpha$ -[H-66dmbp][Hca]		8	6	Chem. Eur. J. 2014, 20, 17515.
<b>P1</b>	12 (off state) 53 (on state)	2	<b>1.9</b>	<b>This Work</b>

### References:

- 1) D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Oxford, 1980.
- 2) A. Mukherjee and S. Ghosh, *Chem. Eur. J.*, 2020, **26**, 12874.

**Author's contribution:** S. Bandyopadhyay synthesized P1 and carried out all experiments related to self-assembly under the supervision of SG. S. Barman carried out all experiments related to ferroelectricity and SP carried out piezoelectricity experiments under the supervision of AD. SG and AD jointly conceptualized the project, and raised research funding. The manuscript was written through contributions of all authors.